# A1: Methods, in-situ δ34S via LA-ICP-MS

The quantitative in-situ analysis of 34S/32S ratios was performed at the MAGMA Lab of the TU Berlin using a Teledyne Analyte Excite 193 nm excimer laser coupled to an Agilent 8900 ICP-MS/MS. Helium was used as a carrier gas at a total flow rate of 0.8 l/min (0.5 l/min cell flow, 0.3 l/min cup flow). After plasma ignition and the start of the He flow, m/z = 42 (e.g. 14N14N14N+) and m/z = 31 (e.g. 15N16O) were recorded to monitor the amount of air entrained in the interface tubing and ablation cell. After the count rate was stable and below 20 000 cps, the nebulizer gas flow was tuned to achieve m/z = 248/232 ratios of < 0.2 % (ThO/Th) and m/z = 232/238 ratios of 100 ± 1 % (Th/U), while ablating NIST 610 in linescan mode. A stable plasma conditions were achieved, an automatic lense tune was performed on NIST 610 to maximize sensitivity in the mid mass range. The resulting tuning parameters are summarized in TableA6. To avoid interferences of molecular ions on m/z = 32 (e.g. 16O16O+ and 14N18O+) and m/z = 34 (18O16O +and 15N18OH+), sulfur isotopes were measured in mass shift mode using an O2 filled reaction cell and O2 flow rates of 0.165 ml/min. Reaction with oxygen produces sulfur species at m/z = 48 (32S16O+) and m/z = 50 (34S16O+), which are denoted as ~32S and ~34S in the following. The O2 flow rate was adjusted, such that both ~32S and ~34S were consistently below <1 MM cps to keep the detector in pulse mode (above 1 MM cps the detector switches to analogue mode; Hans Kavka from Agilent, pers. communication), while ablating pyrite (Fig. A8). To maximize the spatial resolution, the analysis was performed in spot mode using a 50 µm spot size at a repetition rate of 10 Hz. The fluence was tuned based on a series of 300 µm line scans (scan speed: 10 µm/s) of a natural pyrite grain. The sensitivity (in cps) and relative standard deviation (RSD) of the 32S mass channel were recorded as a function of fluence (0.62- 5 J/cm2). A fluence of 1.5 J/cm2 yielded the lowest RSD, which was well above the ablation threshold. Ratios of the two sulfur isotopes 34S/32S are reported in the common delta notation as:

$ \_{ }^{ }$(1)

with (34S/32S)corrected being the average of the measured and background corrected ~34S/~32S ratios. Background correction was done by subtracting the mean ~34S/~32S ratio of the gas blank within 5 seconds before the onset of laser ablation (Fig. A8)

The δ34S values of the unknowns were corrected for instrumental mass bias (MB, equation 2) using the drift-corrected average δ34S value of repeated measurements (n= 27-30) of the balmat pyrite reference material ($δ\_{measured(RM)}$). For δ34Sexpected(RM) the value 15.1 ± 0.2 ‰ from Crowe and Vaughan (1996) was used.

$MB=δ\_{measured(RM)}-δ\_{expected(RM)}$ (2)

$δ\_{corr\left(sample\right)}=δ\_{measured\left(sample\right)}-MB$ (3)

Additionally, balmat sphalerite was used as a secondary standard (δ34Sexpected(RM) = 14.3 ± 0.2 ‰; Crowe and Vaughan 1996). Both ~32S and ~34S were measured with a dwell time of 50 ms. In order to monitor whether phases other than pyrite have been sampled downhole, 75As, 59Co (dwell times 10 ms) and 56Fe (5 ms) were included in the mass scan. This resulted in a total sweep time of 135 ms. Sample analyses were recorded in standard bracketing mode applying the following sequence: balmat pyrite (n=3) – balmat sphalerite (n=1) – unknowns (n=5) – balmat pyrite (n=3) – balmat sphalerite (n=1). The total analysis time of each spot was set to 210s and consisted of 30s gas blank, 90s of ablation and 90s of washout. For calculating the average (34S/32S)corrected value, the first 5 s of the signal were ignored due to insufficient stability, resulting in a total of 407 individual mass sweeps.

To achieve stable ~34S/~32S ratios throughout the interval of signal integration time (electronic supplement Fig. A8), a PFA squid and a homemade Tygon coil were installed between the ablation cell outlet and the torch. The squid device consists of 10 separate 4 mm (OD) PFA tubings of which each has a different length between 25-45 cm. At the squid inlet the sample aerosol is split up and travels in paths of different curvature before it re-mixes at the squid outlet, which is in 33.5cm cm distance to the inlet. The squid significantly improves the washout speed and reduces the measurement uncertainty from 13.3 ‰ to 7.6 ‰ (1 RSDmean). The coil device is homemade and consist of 1.02 mm (ID) Tygon tubing wrapped around 1 cm plastic vial in 8 windings. It has been placed between the squid and the aerosol outlet and further reduced measurement uncertainty down to <1.7 ‰. Similar positive effects of squid and coil on measurement uncertainty have been observed in Gilbert et al. (2014). Both the uncertainty of δ34Smeasured(RM) and δ34Sexpected(RM) contribute less than 8 % to the total measurement uncertainty and are considered to be negligible.

Measurements were performed in two sessions lasting 300 (session 1) and 260 minutes (session 2), respectively. A drift of 1.9 ‰ (session 1) and 2.8 ‰ (session 2) per hour occurred and was corrected for using a linear drift correction based on the repeated measurement of the balmat pyrite. Within the session, reproducibility (estimated from the RSD of drift corrected measurements of δ34SVCDT of the balmat pyrite divided by √n) is <0.7 ‰. Measurement of the balmat sphalerite resulted in δ34Scorr(sample) values of 14.7 ± 1.6 ‰ (1 RSDmean , n= 10, session 1) and 13.6 ± 1.7 ‰ (1 RSDmean, n= 9, session 2) indicating good accuracy and day-to-day reproducibility of the method. Downhole fractionation is considered to be negligible as no significant difference in the mean δ34Scorr(sample) values of the balmat sphalerite has been observed comparing analyses recorded in spot (14.3 ± 1.5, 1 RSDmean, n=10) and linescan mode (14.8 ± 1.8 ‰, 1 RSDmean , n=10).